

## 双核 Fe 配合物 $[(\eta^5\text{-C}_5\text{H}_4)\text{C}_6\text{H}_{10}(\text{C}_4\text{H}_3\text{S})\text{Fe}(\text{CO})_2]_2$ 的合成和晶体结构

田利娟<sup>1</sup> 马志宏<sup>2</sup> 刘晓焕<sup>1</sup> 韩占刚<sup>1</sup> 郑学忠<sup>1</sup> 林 进<sup>\*1</sup>

(<sup>1</sup> 河北师范大学化学与材料科学学院, 石家庄 050016)

(<sup>2</sup> 河北医科大学基础医学院, 石家庄 050017)

**摘要:** 由侧链带有噻吩的环戊二烯基配体  $\text{C}_5\text{H}_5\text{C}_6\text{H}_{10}\text{C}_4\text{H}_3\text{S}$  与  $\text{Fe}(\text{CO})_5$  在二甲苯中加热回流, 合成了 1 个新颖的四羰基二铁配合物  $[(\eta^5\text{-C}_5\text{H}_4)\text{C}_6\text{H}_{10}(\text{C}_4\text{H}_3\text{S})\text{Fe}(\text{CO})_2]_2$ 。通过元素分析、IR、 $^1\text{H}$  NMR 对其结构进行了表征, 用 X-射线单晶衍射确定了其结构。X-射线单晶衍射表明配合物中有 2 个桥羰基和 2 个端羰基, Fe-Fe 的键长为 0.254 65(10) nm。

**关键词:** 羰基铁; 结构; 环戊二烯基; 合成

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## Synthesis and Crystal Structure of Binuclear Iron Complex

### $[(\eta^5\text{-C}_5\text{H}_4)\text{C}_6\text{H}_{10}(\text{C}_4\text{H}_3\text{S})\text{Fe}(\text{CO})_2]_2$

TIAN Li-Juan<sup>1</sup> MA Zhi-Hong<sup>2</sup> LIU Xiao-Huan<sup>1</sup> HAN Zhan-Gang<sup>1</sup> ZHENG Xue-Zhong<sup>1</sup> LIN Jin<sup>\*1</sup>

(<sup>1</sup> College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang 050016, China)

(<sup>2</sup> College of Basic Medicine, Hebei Medical University, Shijiazhuang 050017, China)

**Abstract:** The reaction of the thienyl side chain functionalized cyclopentadienyl ligand  $\text{C}_5\text{H}_5\text{C}_6\text{H}_{10}\text{C}_4\text{H}_3\text{S}$  with  $\text{Fe}(\text{CO})_5$  in refluxing xylene gave the novel cyclopentadienyl tetracarbonyl diiron compound  $[(\eta^5\text{-C}_5\text{H}_4)\text{C}_6\text{H}_{10}(\text{C}_4\text{H}_3\text{S})\text{Fe}(\text{CO})_2]_2$ . The structure of the compound was characterized by elemental analysis, IR,  $^1\text{H}$  NMR spectra and X-ray single crystal diffraction. The X-ray crystal structure indicates the structure with bridging and terminal CO groups and the bond length of Fe-Fe is 0.254 65(10) nm. CCDC: 768950.

**Key words:** carbonyl iron; structure; cyclopentadienyl; synthesis

The coordination chemistry of the cyclopentadienyl have been extensively studied since the ferrocene has been discovered in 1950s<sup>[1-2]</sup>. Replacement of the hydrogen atoms by other substituents alters both the steric and electronic influences of the  $\eta^5$ -cyclopentadienyl ring, resulting in differing reactivity and stability of the substituted cyclopentadienyl metal complexes<sup>[3]</sup>. Recently, people have turned their attention to the heterocyclics of the side chain of cyclopentadienyl<sup>[4-6]</sup>. But few papers have reported on the bearing pendant

thienyl of the cyclopentadienyl ligand. Compared to the O-donor and N-donor ligands, the coordination ability of S-donor is slightly weak. The S atom of the thienyl maybe coordinate to metal center by  $\eta^1$ <sup>[7-8]</sup>. So the thienyl side-chain-functionalized cyclopentadienyl ligands can coordinate to the metal center by  $\eta^5$  model and by  $\eta^1$  model for S atom. The interest of the novel reaction led us to investigate the reactivity of  $\text{Fe}(\text{CO})_5$  with  $\text{C}_5\text{H}_5\text{C}_6\text{H}_{10}\text{C}_4\text{H}_3\text{S}$  ligand and determined the structure of the product.

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\*通讯联系人。E-mail: linjin64@126.com

## 1 Experimental

### 1.1 General procedures

All procedures were performed under a dry oxygen-free argon atmosphere by using standard Schlenk techniques. A majority of solvents were refined from sodium/diphenyl ketone under an atmosphere of nitrogen. Methylene chloride was distilled over  $P_2O_5$  under nitrogen. Furthermore, the chromatographic spectrum was employed using dichloromethane and petroleum ether as eluent.

IR spectra was recorded as KBr pills with a FTIR 8900 spectrometer. Elemental analysis was performed with a VARIO EL III analyzer and  $^1H$  NMR spectrum was recorded with a Bruker AV 500 instrument. The ligand  $C_5H_5C_6H_{10}C_4H_3S$  was prepared according to the literature<sup>[9]</sup>.

### 1.2 Synthesis of the complex

A mixture of the ligand  $C_5H_5C_6H_{10}C_4H_3S$  (0.920 g, 4.0 mmol) and  $Fe(CO)_5$  (0.7 mL, 5.0 mmol) of the xylene (35 mL) was stirred and refluxed for 14 h. After removal of the xylene, the residue was dissolved and filtered using the methylene chloride. After removal of solvent, the residue was chromatographed on an alumina column using  $CH_2Cl_2$ /petroleum ether ( $V:V=1:2$ ) as

eluent. The dark-red band was collected and gave the compound as dark-red crystals (0.78 g, 57.2%). m.p. 216 °C. Anal. Calc. for  $C_{34}H_{34}O_4Fe_2S_2$ (%): C, 59.82; S, 9.38; H, 5.02. Found(%): C, 59.85; S, 9.35; H, 4.98. IR ( $\nu_{CO}$ ,  $cm^{-1}$ ): 1 944s (terminal CO), 1 763s (bridging CO).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  1.36~1.72 (m, 20H,  $(CH_2)_5$ ), 4.09 (m, 4H,  $C_5H_4$ ), 5.85 (m, 4H,  $C_5H_4$ ), 6.96 (d,  $J=2.0$  Hz, 2H,  $C_4H_3S$ ), 7.00 (m, 2H,  $C_4H_3S$ ), 7.15 (d,  $J=6.0$  Hz, 2H,  $C_4H_3S$ ).

### 1.3 Crystal structure determination

The suitable single crystal of compound  $C_{34}H_{34}O_4Fe_2S_2$  was prepared in the solvents of hexane/ $CH_2Cl_2$  ( $V:V=1:2$ ) which slowly volatilized at room temperature. The crystal data of the title compound was collected at 298(2) K with a Bruker Smart Apex CCD diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation ( $\varphi$ - $\omega$  scans,  $\lambda=0.071\ 073$  nm). A total of 7 463 reflections were collected and 2 643 were unique ( $R_{int}=0.028\ 4$ ), of which 2 468 were observed ( $I>2\sigma(I)$ ). The structure was solved by direct methods with SHELXS-97 program and refined with SHELXL 97 by full-matrix least-squares techniques on  $F^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Crystallographic data is summarized in Table 1.

CCDC: 768950.

Table 1 Crystal data and structure refinement for the title complex

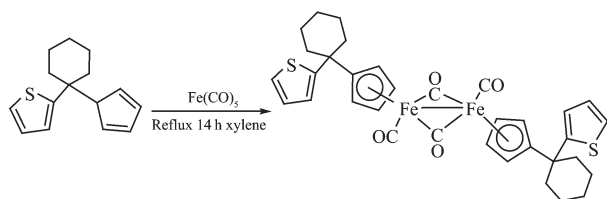
Empirical formula	$C_{34}H_{34}O_4Fe_2S_2$	$F(000)$	708
Formula weight	682.43	Crystal size / mm	0.46×0.34×0.21
Temperature / K	298(2)	$\theta$ range for data collection / (°)	2.84 to 25.01
Wavelength / nm	0.071 073	Limiting indices	$-8 \leq h \leq 8, -32 \leq k \leq 32, -5 \leq l \leq 9$
Crystal system	Monoclinic	Reflections collected / unique ( $R_{int}$ )	7 463 / 2 643 (0.028 4)
Space group	$P2_1/n$	Completeness to $\theta=25.01^\circ$ / %	98.00
$a$ / nm	0.743 25(14)	Absorption correction	Semi-empirical from equivalents
$b$ / nm	2.765 2(5)	Max. and min. transmission	0.790 and 0.639
$c$ / nm	0.785 02(14)	Refinement method	Full-matrix least-squares on $F^2$
$\beta$ / (°)	108.659(2)	Data / restraints / parameters	2 643 / 830 / 271
$V$ / nm <sup>3</sup>	1.528 6(5)	Goodness of fit on $F^2$	1.012
$Z$	2	Final $R$ indices ( $I>2\sigma(I)$ )	$R_1=0.055\ 2, wR_2=0.185\ 5$
$D_c$ / (g·cm <sup>-3</sup> )	1.483	$R$ indices (all data)	$R_1=0.058\ 5, wR_2=0.189\ 2$
$\mu$ / mm <sup>-1</sup>	1.123	Largest diff. peak and hole (e <sup>-</sup> ·nm <sup>-3</sup> )	536 and -675

## 2 Results and discussion

### 2.1 Synthesis of complex

When the ligand  $C_5H_5C_6H_{10}C_4H_3S$  reacted with

$Fe(CO)_5$  in refluxing xylene for 14 h, the corresponding Fe-Fe bonded dinuclear complex  $[(\eta^5-C_5H_4)C_6H_{10}(C_4H_3S)Fe(CO)_2]_2$  was synthesized. The equation of the reaction is followed (Scheme 1).

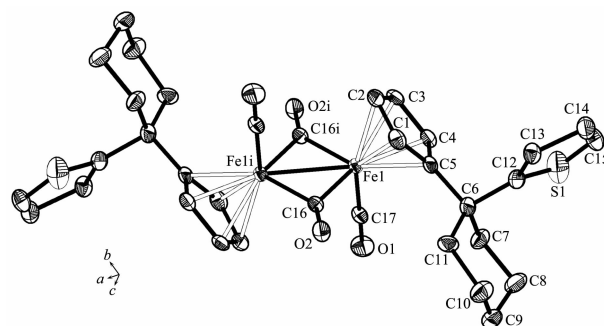


Scheme 1 Synthesis of the title complex

The IR spectrum of diiron complex showed two strong CO absorption peaks at  $1\,944\text{ cm}^{-1}$  in the terminal  $\nu(\text{CO})$  region and one at  $1\,763\text{ cm}^{-1}$  in the bridging  $\nu(\text{CO})$  region. The  $^1\text{H}$  NMR spectrum showed three groups of peaks for the thienyl protons, two groups for the cyclopentadienyl protons, and a group of multiple peaks for the cyclohexyl protons. The results agreed with the single crystal structure.

## 2.2 Crystal structure of the complex

Selected bond lengths and angles are listed in Table 2. The crystal structure of the compound (Fig.1) indicates that it has a *trans* conformation with two bridging carbonyl ligands and two terminal carbonyl ligands. Besides, the conformation of the cyclohexyl ring is a very steady chair form. And the thienyl rings don't involve in coordination with the iron atoms. The two cyclopentadienyl rings and the two thienyl rings are parallel, respectively. At the same time, the structure is symmetrical ( $C_i$ ) and is similar to the *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\mu\text{-CO})]_2$ <sup>[11]</sup>. The bond distance data of the Fe-Fe is  $0.254\,65(10)\text{ nm}$ , which is little longer than *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\mu\text{-CO})]_2$  ( $0.249\,0\text{ nm}$ )<sup>[10]</sup> and *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})(\mu\text{-CO})]_2$  ( $0.253\,4(4)\text{ nm}$ )<sup>[11]</sup>, and is much shorter than *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{Ph})\text{Fe}(\text{CO})(\mu\text{-CO})]_2$  ( $0.256\,35(6)\text{ nm}$ )<sup>[12]</sup> and *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{PhOMe})\text{Fe}(\text{CO})(\mu\text{-CO})]_2$  ( $0.256\,30(8)\text{ nm}$ )<sup>[12]</sup>. The bond distance data show that the thienyl should have small steric



Symmetry code:  $i: -x+2, -y+2, -z+2$ ; Displacement ellipsoids are drawn at the 30% probability level

Fig.1 Molecular structure of the title complex

hindrance.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to refined atoms were placed in geometrically idealized positions and refined using a riding model. The cyclohexyl and thienyl were disordered over two orientations, with refined site occupation factors of  $0.704(6):0.296(6)$ . The C-C bond and C-S bond lengths of the disordered cyclohexyl and thienyl were restrained to be the same within a standard deviation of  $0.001\text{ nm}$ . The ADPs of C7' C8' C9' C10' and C11' were restrained to be same within a standard deviation of  $0.001\text{ nm}$ , the ADPs of C7 C8 C9 C10 and C11 were restrained to be same within a standard deviation of  $0.001\text{ nm}$ . The ADPs of C13 C14 C15 and S1 were restrained to be same within a standard deviation of  $0.001\text{ nm}$ , the ADPs of C13' C14' C15' and S1' were restrained to be same within a standard deviation of  $0.001\text{ nm}$ .

In conclusion, a novel compound with the thienyl ring has been synthesized and characterized by the X-ray single crystal diffractometer. The structure is

Table 2 Bond distances (nm) and angles ( $^\circ$ ) for the title complex

Fe(1)-Fe(1i)	0.254 65(10)	Fe(1)-C(3)	0.212 7(4)	Fe(1)-C(16)	0.192 3(3)
Fe(1)-C(1)	0.213 5(4)	Fe(1)-C(4)	0.210 7(4)	Fe(1)-C(17)	0.175 7(4)
Fe(1)-C(2)	0.212 4(4)	Fe(1)-C(5)	0.213 8(4)		
C(1)-Fe(1)-Fe(1i)	116.83(11)	C(2)-Fe(1)-C(1)	38.80(18)	C(17)-Fe(1)-C(1)	137.74(18)
C(3)-Fe(1)-C(1)	64.55(16)	C(17)-Fe(1)-C(16)	94.52(16)	C(1)-Fe(1)-C(5)	38.26(16)
C(17)-Fe(1)-Fe(1i)	94.38(12)	C(2)-Fe(1)-C(5)	64.77(15)	C(16)-Fe(1)-Fe(1i)	48.81(10)
O(2)-C(16)-Fe(1)	139.4(3)	Fe(1)-C(16)-Fe(1i)	82.67(13)	C(17)-Fe(1)-C(5)	102.09(16)

Symmetry code:  $i: -x+2, -y+2, -z+2$ .

similar to the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\mu\text{-CO})]_2$ , which has a *trans* conformation with two bridging carbonyl ligands and two terminal carbonyl ligands. The difference of the substituents has a little influence on the Fe-Fe bond length.

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